



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : D21H 21/14, B31F 1/12, D21H 23/56, 17/72	A2	(11) International Publication Number: WO 00/09806 (43) International Publication Date: 24 February 2000 (24.02.00)
(21) International Application Number: PCT/US99/18487 (22) International Filing Date: 12 August 1999 (12.08.99) (30) Priority Data: 09/135,428 17 August 1998 (17.08.98) US (71) Applicant: HERCULES INCORPORATED [US/US]; Hercules Plaza, 1313 North Market Street, Wilmington, DE 19894-0001 (US). (72) Inventor: ALLEN, Anthony, John; 1116 Elderon Drive, Arundel, Wilmington, DE 19808 (US). (74) Agent: KULLER, Mark, D.; Hercules Incorporated, Hercules Plaza, 1313 North Market Street, Wilmington, DE 19894-0001 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: CREPING COMPOSITIONS AND PROCESSES		
(57) Abstract <p>Composition comprising at least one water soluble polymer, such as polyamidoamine-epichlorohydrin resin, polyamine-epichlorohydrin resin, polyvinyl alcohol, etc. and at least one stabilizer, such as hypophosphorous acid, phosphorous acid, hypodiphosphoric acid, etc. and salts thereof, suitable as creping adhesive for paper.</p>		

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Creping Compositions and Processes

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to stabilizer for creping adhesives and more particularly it relates to a creping composition comprising water soluble polymer and stabilizer comprising certain acids or salts thereof.

Description of the Prior Art

The creping process is commonly practiced in the manufacture of tissue and towel grades of paper. This process involves scraping the dried paper web from a drying cylinder (Yankee dryer) by the use of a creping doctor blade. The creping action imparts a fine, rippled texture to the sheet and also increases the bulk of the sheet, resulting in improved softness and absorbency. An adhesive formulation is often used to control the adherence of the paper sheet to the Yankee dryer. In this regard, fibrous webs, particularly paper webs, are conventionally subjected to the creping process in order to give them desirable textural characteristics, such as softness and bulk. The creping process typically involves applying creping adhesive - generally in the form of an aqueous solution, emulsion or dispersion - to a drying surface for the web; preferably, this surface is the surface of a rotating creping cylinder, such as the apparatus known as a Yankee dryer. The web is then adhered to the indicated surface. It is subsequently dislodged from the surface with a creping device - preferably, a doctor blade. The impact of the web against the creping device ruptures some of the fiber-to-fiber bonds within the web, causing the web to wrinkle or pucker. The creping adhesive solution, emulsion or dispersion can be comprised of one or more adhesive components, typically water-soluble polymers, and may also contain one or more release agent components as well as other desired additives that may affect the creping process. This is known as the creping adhesive package. This adhesive is exposed to high temperatures (on the order of 100°C) and

high mechanical shear at the creping blade. Given these conditions, one could expect the adhesive formulation to undergo thermooxidative degradation in the presence of atmospheric oxygen. In fact, dark gummy deposits are sometimes observed on the creping blade or Yankee dryer.

5 These deposits are probably thermooxidative degradation products of the creping adhesive formulation and can cause disruptions in the papermaking process. The present invention describes additives for the creping adhesive formulation that significantly reduce the degradation of the creping adhesive formulation under its expected use conditions.

10 Espy & Maslanka, U.S. Patent 5,388,807 and Espy & Giles, Canadian Patent 979,579 disclose polyamidoamine-epichlorohydrin resins (PAE resins) as adhesives in the creping process for producing tissue and towel paper products.

15 A number of patents disclose the use of hypophosphorous acid and its salts as an antioxidant in polymeric formulations. These include Papero, U.S. Patent 3,242,134 disclosing use as a stabilizer for polyamides, Yoshitomi, Nagakura and Matsunuma, Japanese Patent 12,997 disclosing use as an antioxidant in the preparation of alkyd resins, Schuler, Swiss Patent 326,175 disclosing use as a light stabilizer for poly(vinyl chloride) and French Patent
20 1,391,335 (Imperial Chemical Industries Ltd.) disclosing use as a stabilizer in the preparation of polyurethane foams.

The polymers described in the prior art as stabilized by hypophosphorous acid and its salts are all water-insoluble materials. There is no indication given in the prior art that these stabilizers would work in an
25 aqueous system with a water-soluble polymer.

Chen U.S. 4,883,564 discloses a creping adhesive comprising water-soluble binder (polyvinyl alcohol) and a phosphate salt in order to reduce the hard film build up on the creping surface of the drum dryer.

There is no disclosure in the above references of additives used to
30 impart thermal stability to the creping adhesive compositions.

There is no mention in the above references of oxidative instability neither of polyamidoamine-epichlorohydrin or polyamine-epichlorohydrin resins nor of the use of hypophosphorous acid and its salts as stabilizers for polyamidoamine-epichlorohydrin or polyamine-epichlorohydrin creping adhesives.

SUMMARY OF THE INVENTION

According to the present invention there is provided a composition comprising at least one water soluble polymer selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine epichlorohydrin resin, polyacrylamide, polyvinyl alcohol, polyvinylamine, polyethyleneimine, polymethacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(hydroxyethyl acrylate), poly(hydroxyethyl methacrylate), poly(n-vinyl pyrrolidinone), poly(ethylene oxide), hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, starch, agar, chitosan, alginic acid, carboxymethyl cellulose, highly branched polyamidoamines and silylated polyamidoamines; and at least one stabilizer selected from the group consisting of hypophosphorous acid, phosphorous acid, hypodiphosphoric acid, diphosphorous acid, hypophosphoric acid, pyrophosphorous acid and salts of any of these acids.

Further provided according to the present invention are creping adhesives comprising at least one of the above water soluble polymers and at least one of the above stabilizers.

Provided according to the present invention there are processes of forming creped paper comprising : (a) applying the water soluble polymer and stabilizer of the present invention to a drying surface for fibrous web, (b) pressing a fibrous web against the drying surface to adhere the fibrous web to the drying surface, and (c) dislodging the fibrous web from the drying surface with a creping device to crepe the fibrous web.

DETAILED DESCRIPTION OF THE INVENTION

Surprisingly it has been discovered that certain acids, such as phosphorous acid, hypophosphorous acid etc. and their salts are effective

additives in preventing thermal degradation of water soluble polymers, e.g., polyamidoamine-epichlorohydrin and polyamine-epichlorohydrin resins. This type of stabilizer should be useful in the manufacture of tissue papers and paper toweling by providing a more stable creping adhesive coating on the

5 Yankee dryer.

In the context of the present application the term "polymer" is intended to include homopolymers as well as copolymers.

The stabilizers have been shown to be effective in reducing color formation and charring of water soluble polymers, such as polyamidoamine-epichlorohydrin and polyamine-epichlorohydrin resins at levels of about 1 to
10 5%.

The water soluble polymer suitable for the present invention can be selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine epichlorohydrin resin, polyvinyl alcohol, polyvinylamine,
15 polyethyleneimine, acrylamide polymers, polymethacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(hydroxyethyl acrylate), poly(hydroxyethyl methacrylate), poly(n-vinyl pyrrolidinone), poly(ethylene oxide), hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, starch, agar, chitosan, alginic acid, carboxymethyl cellulose, highly branched polyamidoamines and their
20 reaction product with epichlorohydrin and silylated polyamidoamines. Preferably the water-soluble polymer is selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine-epichlorohydrin resin, highly branched polyamidoamines, silylated polyamidoamines, polyvinyl alcohol, polyvinylamine, polyethyleneimine, acrylamide polymers, poly(N-vinyl
25 pyrrolidinone), hydroxyethylcellulose and carboxymethylcellulose, and most preferably they are selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine-epichlorohydrin resin, highly branched polyamidoamines, silylated polyamidoamines, polyvinyl alcohol, polyvinylamine and polyethyleneimine.

30 The stabilizer is selected from the group consisting of hypophosphorous acid, phosphorous acid, hypodiphosphoric acid,

diphosphorous acid, hypophosphoric acid, pyrophosphorous acid and salts of any of these acids. Preferably the stabilizer is hypophosphorous acid, phosphorous acid, hypodiphosphoric acid, diphosphorous acid, hypophosphoric acid, pyrophosphorous acid, sodium hypophosphite, potassium hypophosphite, lithium hypophosphite, calcium hypophosphite, manganese hypophosphite, magnesium hypophosphite, ammonium hypophosphite, phosphorous acid sodium salt, phosphorous acid potassium salt, phosphorous acid lithium salt, phosphorous acid calcium salt, phosphorous acid magnesium salt, phosphorous acid manganese salt and phosphorous acid ammonium salt and most preferably the acidic compound is hypophosphorous acid, phosphorous acid, sodium hypophosphite, potassium hypophosphite, manganese hypophosphite, ammonium hypophosphite, phosphorous acid sodium salt, phosphorous acid potassium salt and phosphorous acid ammonium salt.

The water soluble polymer can be present in an amount of at least about 25% based upon the weight of composition, and preferably at least about 50%. The water soluble polymer can be present in an amount of up to about 99.99%, preferably up to about 99.75%. The stabilizer can be present in an amount of at least about 0.01%, preferably in an amount of at least about 0.25%. The stabilizer can be present in an amount of up to about 75%, preferably in an amount of up to about 15%. Additional components of the creping package may be the creping release agents disclosed in US Patent 5,660,687 (Allen and Lock) the disclosure of which reference is hereby incorporated by reference in its entirety. Suitable release agents include, for example, aliphatic polyols or oligomers thereof having a number average molecular weight of less than 600, polyalkanolamines, aromatic sulfonamides, pyrrolidone, and mixtures thereof. Specific examples of release agents include, for example, ethylene glycol; propylene glycol; diethylene glycol; glycerol; pyrrolidone; triethanolamine; diethanolamine; polyethylene glycol; dipropylene glycol; Uniplex 108, an aromatic sulfonamide available from Unitex Chemical Corporation, Greenville, NC, USA, and mixtures thereof.

Other components of the creping package may also be the polyalkanoamide tackifiers described WO 99/02486, the disclosure of which is incorporated by reference. In addition, the creping adhesive composition can contain release agents, (typical oil-based formulations) surfactants, dispersants, salts to
5 adjust the water hardness, acids or bases to adjust the pH of the creping adhesive composition or other useful additives. The use of such adhesive formulations can provide improved product quality and better control of the papermaking process.

The addition of the various phosphorous or hypophosphorous acids or
10 their salts to formulations of typical polyamidoamine-epichlorohydrin and polyamine-epichlorohydrin creping adhesives has markedly improved thermooxidative stability of these materials. Visual examination of samples that were subjected to high temperatures (150 or 200°C) for 30 minutes showed that the formulations that included 1 to 5% hypophosphite or
15 phosphorous acid were much lighter in color than the control samples. The control samples acquired a very dark brown charred appearance while the samples with added stabilizer were light to golden yellow in color. The resistance of the stabilized formulations to darkening and charring indicate an improvement in the thermooxidative stability of the creping adhesive
20 formulation. Thus one would expect increased durability and stability of a creping adhesive composition containing the stabilizers of this invention, which would be expected to result in improved performance of the paper machine and possibly, improved product quality. The compositions of the present invention may also be advantageous in providing improved creping
25 performance at higher paper machine speeds. This ability to reduce color formation in creping adhesive compositions has also been quantified by a spectrophotometric technique, which is discussed in the Examples.

The composition of the present invention can be used advantageously in the process of creping paper. The creping process according to the present
30 invention can include the steps of applying the stabilizer and creping adhesive either separately or combined, preferably combined as the creping adhesive

package to a drying surface for fibrous web, providing a fibrous web, pressing the fibrous web against the drying surface to adhere this web to the surface, and dislodging the fibrous web from the drying surface with a creping device to crepe the fibrous web.

5 The various hypophosphorous and phosphorous acids and their salts will also improve the thermooxidative stability of other synthetic, naturally occurring or synthetically-modified natural water-soluble polymers and copolymers such as polyvinyl alcohol, polyvinylamine, polyethyleneimine, polyacrylamide, polymethacrylamide, poly(acrylic acid), poly(methacrylic
10 acid), poly(hydroxyethyl acrylate), poly(hydroxyethyl methacrylate), poly(n-vinyl pyrrolidinone), poly(ethylene oxide) [poly (ethylene glycol)], hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), guar gum, starch, agar, chitosan, alginic acid, and carboxymethyl cellulose (CMC). Other useful water-soluble polymers are the highly branched polyamidoamines and their reaction
15 product with epichlorohydrin disclosed in U.S. Patent 5,786,429, (Allen Case 2) the disclosure of which reference is hereby incorporated by reference in its entirety. These polyamidoamines are preferably characterized by a highly branched structure that lacks the reactive intralinker functionality of the wet strength and creping adhesive resins in the prior art. This highly branched
20 structure results from reacting a prepolymer of controlled molecular weight – especially a prepolymer of predetermined low molecular weight – with the requisite amount of epichlorohydrin or other intralinking agent.

 Further these intralinked polyamidoamines are preferably nonthermosetting and endcapped intralinked polyamidoamines. Also as a
25 matter of preference, the intralinked polyamidoamines are free or substantially free of reactive intralinker functionality.

 The intralinked polyamidoamines preferably comprise the reaction product of reactants which include at least one dicarboxylic acid or dicarboxylic acid derivative, at least one polyamine, at least one endcapping
30 agent, and at least one intralinker. The at least one endcapping agent preferably comprises at least one member selected from the group consisting

of monofunctional amines, monofunctional carboxylic acids, and monofunctional carboxylic acid esters.

Further the intralinked polyamidoamines preferably comprise the reaction product of an endcapped polyamidoamine prepolymer and the at least one intralinker. The endcapped polyamidoamine prepolymer itself preferably comprises the reaction product of the at least one dicarboxylic acid or dicarboxylic acid derivative, the at least one polyamine, and the at least one endcapping agent.

Also as a matter of preference, the endcapped polyamidoamine prepolymer is free or substantially free of amine and carboxyl end groups. Additionally, the endcapped polyamidoamine prepolymer preferably comprises alternating dicarboxylic acid and polyamine residues, and endcaps lacking carboxyl and amine functionality; yet further, the endcaps are preferably amide endcaps.

The endcapped polyamidoamine prepolymer preferably has a DP_n of about 2 to about 50 – more preferably about 3 to about 25, and still more preferably about 3 to about 10. Also as a matter of preference, the mole ratio of the at least one intralinker, to intralinker reactive amine groups in the endcapped polyamidoamine prepolymer, is between about $\frac{1}{2} [1/(DP_n - 1)]$ and about $1/(DP_n - 1)$. Also useful as the water-soluble polymers are the silyl-linked polyamidoamines disclosed in EP 0 814 108, the disclosure of which reference is hereby incorporated by reference in its entirety.

Preferably, the silyl-linked polyamidoamines are thermosetting. Also as a matter of preference, they are soluble in an aqueous medium.

These silylated polyamidoamines can comprise the reaction product of reactants which comprise at least one dicarboxylic acid or dicarboxylic acid derivative, at least one polyamine, and at least one silylating agent. The reactants further can comprise at least one cationizing agent, and/or at least one endcapping agent.

Particularly, the silylated polyamidoamines can comprise the reaction product of the at least one silylating agent, and a polyamidoamine prepolymer comprising the reaction product of the at least one dicarboxylic acid or dicarboxylic acid derivative and the at least one polyamine; the reactants for
5 preparing the prepolymer can also include at least one endcapping agent. Preferably, the at least one silylating agent comprises at least one functionality capable of reacting with amine groups in the polyamidoamine prepolymer, and at least one hydrolyzable site.

Also as a matter of preference, the mole ratio of the at least one
10 silylating agent, to silylating agent reactive amine groups in the polyamidoamine prepolymer, is between about 0.05 and about 2.0. This mole ratio is more preferably between about 0.1 and about 0.75, and between about 0.15 and about 0.5 as a matter of particular preference.

Other possible uses of the stabilized polymers of the present invention
15 are as improved wet strength agents for paper, in adhesive compositions, as textile fiber treatments, as dispersant, as improved dispersants and/or promotor resins in paper sizing compositions and as components of paper coating formulations.

The scope of the present invention as claimed is not intended to be
20 limited by the following Examples which are given merely by way of illustration. All parts and percentages are by weight unless otherwise indicated.

Examples 1 to 36 and Comparative Examples 1 to 4

In order to test the thermooxidative stability of resin/stabilizer
25 formulations an accelerated aging test was performed which involved heating samples in a forced air oven and then determining their color. Aqueous solutions of Crepetrol® 80E and Kymene® 557LX polyamidoamine-epichlorohydrin resins available from Hercules Incorporated and Crepetrol® 73 polyamine-epichlorohydrin resin available from Hercules Incorporated were
30 mixed with candidate stabilizers and were placed in aluminum weighing pans measuring 55 mm diameter x 15 mm high. The total amount of resin and

stabilizer added was 2.00g. The resin formulations were dried in a forced air oven for 30 minutes at either 150°C or 200°C. After removing from the oven the samples were stored in a dessicator until the color determinations were performed. Color determination was done with a Spectrogard Color System spectrophotometer made by BYK-Gardner USA. The yellowness of the samples was determined according to ASTM method D-1925-70, standard test method for yellowness index of plastics.

Yellowness index results for Crepetrol® 80E resin/stabilizer combinations are listed in Table 1. Yellowness index results of Kymene® 557LX and Crepetrol® 73 resins in combination with stabilizers are shown in Table 2. Addition of the hypophosphite and phosphorous acid stabilizers reduced the yellowness of all samples significantly at the concentrations tested (1, 2.5 and 5%) and the reduction in the yellowness index was generally directly proportional to the amount of stabilizer added.

Table 1. Crepetrol® 80E Resin/Stabilizer Formulations

Example	Adhesive	Stabilizer	Temp.(°C)	pH ¹	Yellowness Index ²
C-1	C-80E	None (control)	200	3.92	116.0
1	C-80E	1.0% Sodium hypophosphite	200	3.92	58.9
2	C-80E	2.5% Sodium hypophosphite	200	3.93	31.6
3	C-80E	5.0% Sodium hypophosphite	200	3.94	17.0
4	C-80E	1.0% Manganese hypophosphite	200	3.90	57.9
5	C-80E	2.5% Manganese hypophosphite	200	3.87	54.6
6	C-80E	5.0% Manganese hypophosphite	200	3.90	37.6
7	C-80E	1.0% Phosphorous acid	200	3.27	71.6
8	C-80E	2.5% Phosphorous acid	200	2.12	29.7
9	C-80E	5.0% Phosphorous acid	200	1.61	27.3
C-2	C-80E	None (control)	150	3.92	113.3
10	C-80E	1.0% Sodium hypophosphite	150	3.92	86.8
11	C-80E	2.5% Sodium hypophosphite	150	3.93	37.6
12	C-80E	5.0% Sodium hypophosphite	150	3.94	26.8
13	C-80E	1.0% Manganese hypophosphite	150	3.90	90.7
14	C-80E	2.5% Manganese hypophosphite	150	3.87	53.3
15	C-80E	5.0% Manganese hypophosphite	150	3.90	36.7
16	C-80E	1.0% Phosphorous acid	150	3.27	79.7
17	C-80E	2.5% Phosphorous acid	150	2.12	49.7
18	C-80E	5.0% Phosphorous acid	150	1.61	28.2

¹Measured prior to drying.

²Determined by ASTM D-1925-70, Standard Test Method for Yellowness Index of Plastics

Table 2. Kymene® 557LX and Crepetrol® 73 Resins with Stabilizers

Example	Adhesive	Stabilizer	Temp.(°C)	pH	Yellowness Index ¹
C-3	K-557LX	None (control)	150	3.48	111.2
19	K-557LX	1.0% Sodium hypophosphite	150	3.56	84.7
20	K-557LX	2.5% Sodium hypophosphite	150	3.57	80.9
21	K-557LX	5.0% Sodium hypophosphite	150	3.59	60.8
22	K-557LX	1.0% Manganese hypophosphite	150	3.49	96.6
23	K-557LX	2.5% Manganese hypophosphite	150	3.53	85.5
24	K-557LX	5.0% Manganese hypophosphite	150	3.55	79.6
25	K-557LX	1.0% Phosphorous acid	150	2.72	86.8
26	K-557LX	2.5% Phosphorous acid	150	1.99	67.0
27	K-557LX	5.0% Phosphorous acid	150	1.42	76.7
C-4	C-73	None (control)	150	4.02	68.7
28	C-73	1.0% Sodium hypophosphite	150	3.90	52.1
29	C-73	2.5% Sodium hypophosphite	150	3.91	22.0
30	C-73	5.0% Sodium hypophosphite	150	3.97	28.3
31	C-73	1.0% Manganese hypophosphite	150	3.92	42.3
32	C-73	2.5% Manganese hypophosphite	150	3.90	24.2
33	C-73	5.0% Manganese hypophosphite	150	3.87	15.6
34	C-73	1.0% Phosphorous acid	150	2.47	51.4
35	C-73	2.5% Phosphorous acid	150	1.35	65.4
36	C-73	5.0% Phosphorous acid	150	0.83	65.0

¹Determined by ASTM D-1925-70, Standard Test Method for Yellowness Index of Plastics.

What is claimed is:

1. A composition comprising at least one water soluble polymer selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine-epichlorohydrin resin, polyvinyl alcohol, polyvinylamine, polyethyleneimine, polyacrylamide, polymethacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(hydroxyethyl acrylate), poly(hydroxyethyl methacrylate), poly(n-vinyl pyrrolidinone), poly(ethylene oxide), hydroxyethyl cellulose, hydroxypropyl cellulose, guar gum, starch, agar, chitosan, alginic acid, carboxymethyl cellulose, highly branched polyamidoamines and their reaction product with epichlorohydrin and silyl-linked polyamidoamines; and at least one stabilizer selected from the group consisting of hypophosphorous acid, phosphorous acid, hypodiphosphoric acid, diphosphorous acid, hypophosphoric acid, pyrophosphorous acid and salts of any of these acids.

2. The composition of claim 1 wherein the water soluble polymer is selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine-epichlorohydrin resin, highly branched polyamidoamines, silylated polyamidoamines, polyvinyl alcohol, polyvinylamine, polyethyleneimine, acrylamide polymers, poly(N-vinyl pyrrolidinone), hydroxyethylcellulose and carboxymethylcellulose.

3. The composition of claim 1 wherein the water soluble polymer is selected from the group consisting of polyamidoamine-epichlorohydrin resin, polyamine-epichlorohydrin resin, highly branched polyamidoamines, silylated polyamidoamines, polyvinyl alcohol, polyvinylamine and polyethyleneimine.

4. The composition of claims 1-3 wherein the stabilizer is selected from the group consisting of hypophosphorous acid, phosphorous acid, hypodiphosphoric acid, diphosphorous acid, hypophosphoric acid, pyrophosphorous acid, sodium hypophosphite, potassium hypophosphite,

lithium hypophosphite, calcium hypophosphite, manganese hypophosphite, magnesium hypophosphite, ammonium hypophosphite, phosphorous acid sodium salt, phosphorous acid potassium salt, phosphorous acid lithium salt, phosphorous acid calcium salt, phosphorous acid magnesium salt,
5 phosphorous acid manganese salt and phosphorous acid ammonium salt.

5. The composition of claim 4 wherein the stabilizer is selected from the group consisting of hypophosphorous acid, phosphorous acid, sodium hypophosphite, potassium hypophosphite, manganese hypophosphite,
10 ammonium hypophosphite, phosphorous acid sodium salt, phosphorous acid potassium salt and phosphorous acid ammonium salt.

6. The composition of claims 1-5 wherein the water soluble polymer is present in an amount of at least about 25% based upon the weight of the
15 composition.

7. The composition of claim 6 wherein the water soluble polymer is present in an amount of at least about 50% based upon the weight of the composition.

20 8. The composition of claim 1-7 wherein the water soluble polymer is present in an amount of up to about 99.99% based upon the weight of the composition.

25 9. The composition of claim 8 wherein the water soluble polymer is present in an amount of up to about 99.75% based upon the weight of the composition.

10. The composition of claims 1-9 wherein the stabilizer is present in an amount of at least about 0.01% based upon the weight of the composition.

30 11. The composition of claim 10 wherein the stabilizer is present in an amount of at least about 0.25% based upon the weight of the composition.

12. The composition of claim 1-11 wherein the stabilizer is present in an amount of up to about 75% based upon the weight of the composition.

5 13. A creping adhesive comprising the composition of claims 1-12.

14. The creping adhesive comprising the composition of claim 13 further comprising at least one of release agent, surfactant, dispersant, bases and acids and salts other than hypophosphorous acid, phosphorous acid, 10 hypodiphosphoric acid, diphosphorous acid, hypophosphoric acid, pyrophosphorous acid and salts thereof.

15. A process of forming creped paper comprising:

(a) applying the water soluble polymer and stabilizer of the 15 composition of claims 1-12 either separately or combined to a drying surface for fibrous web;

(b) pressing a fibrous web against the drying surface to adhere the fibrous web to the drying surface; and

(c) dislodging the fibrous web from the drying surface with a creping 20 device to crepe the fibrous web.

16. A process of forming creped paper comprising:

(a) applying the creping adhesive of claim 13 to a drying surface for fibrous web;

25 (b) pressing a fibrous web against the drying surface to adhere the fibrous web to the drying surface; and

(c) dislodging the fibrous web from the drying surface with a creping device to crepe the fibrous web.

17. The process of claim 16 wherein the creping adhesive 30 composition further comprises at least one of release agent surfactant, dispersant, bases and acids and salts other than hypophosphorous acid,

phosphorous acid, hypodiphosphoric acid, diphosphorous acid, hypophosphoric acid, pyrophosphorous acid and salts thereof.

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